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(54) **Process for the preparation of a high-purity cobalt intermediate**

Verfahren zur Herstellung von hoch-reinen Cobalt-Zwischenprodukten

Procédé pour la préparation des produits intermédiaires à cobalt de haute pureté

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EP 0 651 062 B1

Description

The present invention resides in a process for the preparation of a high purity cobalt intermediate substantially free of both cationic and anionic impurities. The process allows for a cobalt intermediate to be recovered in high yield and purity from an ammoniacal ammonium carbonate solution of the cobalt tetrammine complex.

In prior art processes nickel and cobalt bearing ores and concentrates may for example be processed by the reduction roast ammonium carbonate oxidative leach route. By this route, impure cobalt sulphide is produced as a by-product, and the isolation and recovery of this by-product is illustrated in Australian Patent AU-B- 605867.

The recovery of cobalt as a sulphide is achieved by injection of a suitable sulphiding agent, for example, gaseous hydrogen sulphide or ammonium hydrosulphide solution. This procedure however results in the precipitation of sulphides of other elements present such as iron, zinc, copper and nickel as well as the adsorption and or coprecipitation of compounds that normally do not produce insoluble sulphides, such as calcium, magnesium and manganese.

In order to produce pure cobalt metal or a pure cobalt compound for industrial applications it is necessary to first solubilize the impure sulphides and then isolate the cobalt in a suitable form free of unwanted impurities.

A number of processes have been reported describing the isolation of cobalt as a pure product. These procedures usually involve a combination of solubilization, precipitation, solvent extraction and electrowinning operations. One such process, known as the Nippon Mining Corporation process, recovers cobalt in the metallic form by electrowinning from an acidic sulphate solution. Another process, known as the Sumitomo process, also recovers cobalt in metallic form however this is electrowon from a chloride solution. Both of these operations have common features in that the cobalt is present in the cobaltous state at the point of isolation and the product is a massive metal cathode plate.

Another commercial cobalt sulphide refining process is the soluble cobaltic ammine process developed by Sherritt Gordon Mines Ltd. This process involves solubilization, precipitation of hydrated ferric oxide, conversion of the cobaltous sulphate to cobaltic pentammine sulphate, precipitation of nickel ammonium sulphate, reduction of the cobaltic pentammine to cobaltous diammine and, finally, pressure hydrogen reduction to cobalt metal powder.

Cobalt has many applications and not all of these require cobalt metal. For example, cobalt salts find use in a variety of industries and significant quantities of cobalt oxide are also used industrially. Consequently, a pure cobalt compound able to be converted to salts, oxides and fine metal powder would be a useful industrial commodity.

The present invention aims to overcome or at least alleviate one or more of the difficulties associated with the prior art.

The present development relates to a suitable method of purifying cobalt by a combination of solubilization, solvent extraction and optionally ion exchange operations that allows cobalt to be recovered from a solution in which it is present in the cobaltic state.

The present invention resides in a process for the preparation of a cobalt intermediate substantially free of both cationic and anionic impurities from impure cobalt sulphide, wherein the process is characterised by solvent extraction in both an acidic medium and basic ammoniacal medium to remove both cationic and anionic impurities.

In particular, in a first aspect, the present invention resides in a process for the preparation and purification of a cobalt intermediate from a cobalt sulphate solution containing cationic and anionic impurities, including the successive steps of:

(i) reacting the cobalt sulphate solution with an organic reagent to extract unwanted cationic impurities from the sulphate solution;

(ii) extracting the cobalt from the sulphate solution with an organic reagent, to create a cobalt loaded organic phase substantially free of all anionic impurities;

(iii) stripping the cobalt loaded organic phase with a high strength ammoniacal ammonium carbonate solution, to create a cobalt rich ammoniacal ammonium carbonate strip liquor rich in cobalt II ammines;

(iv) converting the cobalt II ammines to cobalt III tetrammine;

(v) extracting the majority of nickel from the cobalt tetrammine rich ammoniacal liquor with a suitable organic reagent; and

(vi) recovering the cobalt from the cobalt tetrammine rich ammoniacal liquor.

Most preferably the process also includes a further extraction step wherein further unwanted cationic impurities are removed by contacting the cobalt rich ammoniacal liquor with an ion exchange resin.

The invention is characterised in that the process sequentially treats a cobalt containing solution to remove impu-

urities such as iron, zinc, copper, manganese, nickel, magnesium and calcium and employs an acid/base solvent extraction transfer step to remove anionic impurities such as sulphate, chloride and nitrate. The preferred features of the invention will become evident from the following description.

The process of the invention is particularly applicable to recovering cobalt from insoluble cobalt sulphide solids. The methods available to convert insoluble cobalt sulphide solids to soluble cobalt salts are varied and they generally require the injection of air or oxygen at atmospheric or higher pressure into an aqueous slurry of the solids at elevated temperature. For the purposes of this solubilization step, it is preferred to inject air or oxygen at a temperature range of 60°C to 90°C at atmospheric pressure, the reaction period can be adjusted to achieve the degree of solubilization required. The temperature may be controlled by the circulation of water or steam. The end result is the production of a solution of cobalt sulphate of pH lower than 2.5 with cobalt concentration of 30 to 90 g/l, preferably about 50-65 g/l.

During the dissolution of the cobalt sulphide, the impurity elements present also dissolve. This allows the cobalt solution to be subjected to the appropriate purification steps. The Nippon Mining Corporation, Sumitomo and Sherritt Gordon processes each employ a precipitation step to remove iron as ferric hydroxide from the cobalt sulphate solution. However, when ferric hydroxide precipitates from cobalt-rich aqueous solutions, some cobalt is lost, adsorbed to, or coprecipitated with the ferric hydroxide solids. This represents a cobalt loss that is not easily reversed. Most preferably, the present invention employs an organic reagent or reagents specific for ferric iron and zinc at predetermined pH values to strip any iron and zinc from the solution without any significant loss of cobalt, which avoids the difficulty of the prior art processes.

It is particularly preferred that the organic reagent for the extraction of cationic impurities from the cobalt sulphate solution is specific for the extraction of ferric iron and zinc. It is most desirable that the iron present in the cobalt sulphate solution be ferric (Fe³⁺) ions, and accordingly the cobalt sulphate solution may be treated with a strong oxidant, for example hydrogen peroxide, to convert any iron present to ferric iron.

It should be appreciated that control of pH during solvent extraction is important if complete and selective separations are to be achieved. For the process of the present invention, it is most desired to maintain the pH value of the solution initially between a pH value of less than 2.8, preferably from about 2.1 to 2.6, which will generally separate about 95% of the ferric iron from the solution, and slowly raising the pH to about 3.5 specific for zinc separation. The present invention enables ferric iron and zinc to be selectively and effectively removed in sequence from the acidic cobalt sulphate solution.

A suitable organic reagent for this step has been found to be a phosphinic acid derivative dissolved in a kerosene solvent, for example a preferred reagent is bis(2,4,4-trimethylpentyl)phosphinic acid in aliphatic kerosene (Escaid 110). The ratios of these components may be adjusted to yield the required optimum extraction and stripping properties.

The effectiveness of the removal for iron and zinc from aqueous cobalt sulphate solution utilizing the above procedure is illustrated by the results in Table 1.

TABLE 1

	Co/Fe ratio	Co/Zn ratio
Cobalt Sulphate feed Liquor	100	30
Treated Liquor	40,000	150,000
Loaded Strip Liquor	0.0005	0.0001

Consideration of the nature of the desired high purity cobalt intermediate requires that not only cationic but also anionic impurities need to be removed. It has been found that this may be achieved if the cobalt is transferred from an acidic sulphate medium to a basic ammoniacal ammonium carbonate medium.

In order to transfer the cobalt from the acidic sulphate solution, the cobalt may be extracted with a suitable organic reagent to create a cobalt loaded organic phase. Those familiar with solvent extraction chemistry will appreciate that only cations will chemically be transferred to the organic reagent, while anions will remain with the aqueous phase. Consequently there has been a separation of cobalt from anionic impurities such as sulphate, chloride and nitrate ions.

Most suitably the organic reagent is a phosphoric acid derivative dissolved in kerosene and modified with an aliphatic long chain alcohol. A preferred organic reagent to effect the transfer of cobalt from an acid medium to an ammoniacal ammonium carbonate medium was found to be a mixture of di(2-ethylexyl)phosphoric acid, iso-tridecanol and aliphatic kerosene in suitable proportions to yield optimum extraction and stripping properties.

The reaction generally takes place in mixer settler extraction cells. Some cationic impurities may also transfer to the organic phase.

The cobalt loaded organic reagent exiting the extraction cells may also physically remove some aqueous phase containing sulphate and in order to remove this contamination the cobalt loaded organic reagent may be transferred to mixer settler scrub cells. An aqueous scrub liquor which may be either dilute ammonia, dilute ammonium carbonate

or deionized water is used to contact the organic phase to remove entrained aqueous sulphate, chloride and nitrate impurities.

The cobalt loaded organic phase exiting the scrub cells is transferred to mixer settler strip cells where the cobalt is stripped from the organic phase by high strength ammoniacal ammonium carbonate solution. A solution of composition 205 to 330 g/l ammonium and 160 to 300 g/l carbon dioxide, preferably 255 to 300 g/l ammonia and 200 to 260 g/l carbon dioxide, and most preferably 285 g/l ammonia and 230 g/l carbon dioxide has been found most effective. It should be understood that by varying the ratio of strip liquor to cobalt loaded organic phase, considerable increases in cobalt concentration in the aqueous strip phase can be achieved. The nature of the cobalt rich ammoniacal liquor is illustrated by the data in Table 2.

TABLE 2

	Co	SO ₄ ²⁻
Cobalt Sulphate Feed Liquor	50 g/l	100 g/l
Loaded Ammoniacal Liquor	80 g/l	5 ppm

Nickel may now be removed from the ammoniacal liquor. The separation of nickel from cobalt in ammoniacal carbonate liquors is influenced greatly by two factors:-

(i) the presence of cobalt (II) amines, and

(ii) the ammonia concentration of the cobalt rich liquor.

In order to effectively remove nickel from the cobalt rich ammoniacal liquor produced by the cationic transfer process outlined above, the labile cobalt II amines should be converted to stable cobalt III tetrammine. This is generally achieved by sparging the cobalt rich ammoniacal liquor with air or oxygen and hydrogen peroxide in order to oxidise the cobalt II to cobalt III. During this oxidation step, the cobalt II ammine concentration is generally lowered from about 20 g/l to about 50 ppm. The cobalt III tetrammine rich ammoniacal liquor may be subjected to controlled distillation to lower the uncomplexed NH₃ concentration to approximately 20-60 g/l, preferably about 40 g/l without destabilizing the cobalt ammine and causing precipitation of solids in the distillation column. Cooling of this ammoniacal liquor is preferred to control its temperature prior to transfer to a series of solvent extraction cells to effect nickel removal.

In order to effectively lower the nickel concentration of the cobalt tetrammine rich ammoniacal liquor to a suitably low value, it is preferred to use an organic reagent with very low residual nickel loading. This is a natural consequence of the equilibrium relationship between an element in an organic and aqueous phase in contact.

The most preferred organic reagent used in this step is either an oxime reagent, for example, an acetophenone-oxime or salicylaldoxime, or a substituted beta diketone, in kerosene and modified by the addition of a long chain aliphatic alcohol, for example iso-tridecanol, iso-undecanol, iso-dodecanol, and the corresponding linear type. The preferred reagent is a mixture of 2-hydroxy-5-t-nonyl acetophenoneoxime in aliphatic kerosene modified by the addition of iso-tridecanol. This reagent stream may be contacted with high strength ammoniacal ammonium carbonate liquor, with a typical concentration of from 205 to 330 g/l ammonia, preferably 280 g/l, and 160 to 300 g/l carbon dioxide preferably 230 g/l to remove nickel from the organic reagent. This reaction generally takes place in a series of mixer settler cells at a strip cell temperature of between 35° to 55°C for a period of between 30 seconds and 30 minutes in each cell, preferably 3 minutes.

The nickel free organic reagent may then contact the cobalt III tetrammine rich ammoniacal liquor to remove the nickel impurity from the cobalt liquor. This reaction may be carried out in mixer settlers and the usual factors of organic to aqueous ratio, temperature, residence time in the mixer boxes and numbers of strip and extract cells should be optimized. For example, a suitable organic to aqueous ratio may be 0.2:1 to 5:1, preferably 1:1 to 2:1, at a temperature in the extract cells of between 35°C and 60°C, for period of between 30 seconds and 30 minutes, preferably about 3 minutes.

The effectiveness of this circuit is illustrated by the data presented in Table 3.

TABLE 3

	Co	Ni
Ammoniacal Feed Liquor	60 g/l	1.8 g/l
Treated Liquor	60 g/l	1 ppm

Copper and manganese which are usually present at levels of up to 20 ppm in the ammoniacal feed liquor are

also extracted to residual levels of less than 2 ppm during this extraction.

The cobalt tetrammine rich ammoniacal liquor essentially free of nickel, iron, zinc, copper, manganese, sulphate and chloride ions may then be subjected to filtration through an activated carbon bed (to scavenge any entrained organic reagent removed from the nickel extraction circuit) before being contacted with a suitably conditioned ion exchange resin in order to remove any residual calcium and magnesium.

A number of ion exchange resins were tested, however given the nature of the feed solution and the duty required from the ion exchange resin the most preferred is a chelating ion exchange resin of the Iminodiacetate type with a high affinity for calcium and magnesium. Given the nature of the feed solution, cobalt tetrammine rich with calcium and magnesium in ammoniacal ammonium carbonate, it is most preferred that the resin be conditioned prior to use to avoid the evolution of gas and disruption of the resin bed during operation. It will be appreciated that during ion exchange resin operations, gas evolution may have a detrimental effect on the operating efficiency of an ion exchange system.

For continuous operation three individual ion exchange resin columns are most preferred, two operating in series with the third on standby following regeneration. This enables control of the calcium and magnesium impurities associated with cobalt exiting the ion exchange resin system. The effectiveness of this system is illustrated by the data in Table 4.

TABLE 4

	Co	Mg	Ca
Ammoniacal Feed Liquor	60 gl ⁻¹	200 ppm	50 ppm
Treated Liquor	60 gl ⁻¹	1 ppm	1 ppm

The cobalt rich ammoniacal liquor exiting the ion exchange resin system contains extremely low levels of both cationic and anionic impurities. The cobalt III tetrammine complex while stable at ambient temperatures is readily destroyed at elevated temperatures forming an insoluble cobaltic oxide hydroxide virtually free of any contaminating anions such as sulphate, chloride and nitrate.

In order to recover the cobalt in an intermediate form, in one preferred way, the cobalt tetrammine rich ammoniacal liquor may be delivered continuously under controlled conditions to a multi-tray distillation column heated with steam. The off gases are condensed and recovered while the aqueous slurry is pumped to a thickener to recover the suspended cobaltic oxide hydroxide solids.

These solids because of their composition, particle size and purity are an ideal intermediate from which to prepare a range of cobalt end products.

Typical composition of the cobaltic oxide hydroxide solids produced is given in Table 5.

TABLE 5

	Typical Value %		Typical Value %
Co	64	Mg	0.001
Ni	0.001	Ca	0.001
Fe	0.001	Al	0.001
Cu	0.001	Si	0.001
Zn	0.001	Na	0.001
Mn	0.001	Cl	<0.001

As an alternative step, the cobalt liquor exiting the ion exchange resin system may also be treated in a reductive step by contacting the liquor with finely divided pure cobalt metal powder to reduce the cobalt III tetrammine to labile cobalt II ammine.

This reaction may take place in an inert atmosphere at from 25°C to 35°C and results in the precipitation of cobalt hydroxy carbonate solids. The solution is distilled to recover ammonia and carbon dioxide while driving the precipitation reaction to completion.

According to a second aspect, the present invention also resides in cobalt intermediate compounds, produced by the process of the present invention as outlined above.

By way of example, figure 1 provides a flow diagram of the process according to the present invention. It will be appreciated that this chart is merely illustrative of a preferred embodiment of the invention, and the invention should not be considered limited thereto.

The process flow diagram (Fig 1) for the present invention illustrates the injection of air (1) into four reactor units (A), (B), (C) and (D) and the injection of oxygen (2) into two reactor units (E) and (F) at atmospheric pressure. The

reaction temperature can be controlled at the required value, 60° to 90°C by the circulation of water or steam through appropriately positioned coiled tube. The reaction period can be adjusted to achieve the degree of solubilization of cobalt sulphide solids to soluble cobalt salts required, the liquor leaving the final reaction unit (F) is a solution of cobalt sulphate of pH less than 2.5 units and cobalt concentration varying from 30 to 90 g/l and which is passed through a filter (G) to remove any particulate matter.

For the extraction of cationic impurities, iron and zinc, it is most desired that the iron present in stream (3) exiting filter (G) be treated with a strong oxidant, for example hydrogen peroxide stream (4), to ensure only ferric (Fe^{3+}) ions are present prior to entering the first mixer settler extraction cell (H).

It is also most desired that the oxidised stream (5) during its progress through the mixer settler cells (H) and (I) is maintained at a pH of less than 2.8 units to eliminate the potential for the precipitation of ferric hydroxide within the solvent extraction circuit. For the extraction of zinc also present in stream (5) to go to completion, a pH of 3.5 units is most desired, and therefore a basic reagent injection system (6) is required to maintain all the extraction cells (H), (I), (J) and (K) at the optimum pH to remove in the first case ferric iron and then to remove zinc.

The additional mixer settler cells illustrated in Fig. 1 are required to first remove any entrained cobalt rich aqueous phase from the iron and zinc loaded organic reagent stream (8). Cells (L) and (M) are used for this purpose, the scrub stream (9) used for this purpose may be water. The cobalt free iron and zinc loaded organic reagent (10) exiting scrub cell (M) is then subjected to stripping with dilute sulphuric acid (11) in mixer settler units (N), (O), (P) and (Q) before exiting mixer settler cell (Q) as stream (12) stripped organic reagent. This reagent stream again being available to extract iron and zinc on a continuous basis. Stream (13) is a waste stream containing iron and zinc sulphate.

The cobalt sulphate solution stream (7) essentially free of iron and zinc contaminants, is pumped to mixer settler cell (R) where it is contacted with a suitable volume of an organic reagent mixture, for example, a mixture of di(2-ethyl-hexyl)phosphoric acid, iso-tridecanol and aliphatic kerosene, effecting a transfer of cobalt from the aqueous phase to the organic phase.

Three mixer settler extraction cells (R), (S) and (T) were found adequate to maximise the cobalt extraction and the stream (14) leaving cell (T) is essentially cobalt free. The cobalt loaded organic reagent exiting extraction cell (R) stream (15) may be contaminated with physically associated aqueous liquor containing anionic impurities. Since the object of the above transfer step is to separate cobalt from anionic impurities, it is most preferred to pump the cobalt loaded organic reagent to mixer settler scrub cells where the organic phase is contacted with deionized water (16) to remove impurities. Two scrub cells (U) and (V) are used and the scrub stream containing some cobalt (20) is returned to extraction cell (R) for recovery.

The scrubbed cobalt loaded organic reagent (17) exiting scrub cell (V) enters mixer settler strip cell (W) where it contacts ammoniacal ammonium carbonate strip liquor leaving strip cell (X). This countercurrent progression of organic and aqueous phases continues through the four strip cells (V), (W), (X) and (Y) required to recover the cobalt from the organic reagent. The most suitable liquor for the above described cobalt stripping procedure was found to be one containing 285 g/l of ammonia and 230 g/l of carbon dioxide.

The ammoniacal ammonium carbonate strip liquor stream (18), free of cobalt, enters strip cell (Z) and exits strip cell (W), stream (19) containing approximately 80 g/l cobalt. The cobalt rich liquor stream (19) is pumped to two reactor vessels in series (A1) and (A2) and air and or oxygen (21) injected during vigorous agitation of the liquor to convert cobalt II amines to cobalt III amines.

The oxidised liquor exiting vessel (A2) is agitated in vessel (A3) during the injection of hydrogen peroxide (22) to complete the oxidation cycle. The oxidised liquor (23) will have been depleted in ammonia to some extent as the injection of air will remove free ammonia, the extent of removal depending on the reaction time. The oxidised liquor (23) rich in cobalt III amines may now be subjected to controlled distillation in column (A4) to lower the uncomplexed ammonia concentration to approximately 40 g/l without destabilizing the cobalt amines and causing precipitation in the distillation column. Steam (24) is injected into the column to effect the removal of ammonia. Stream (25) is an off gas stream containing NH_3 , CO_2 and steam and is condensed for recycling.

In order to effectively lower the nickel concentration of the cobalt tetrammine rich ammoniacal liquor exiting the distillation column, stream (26), to a suitably low value, it is preferred to use an organic reagent with very low residual nickel loading. This is a natural consequence of the equilibrium relationship between an element in an organic and aqueous phase in contact.

The most preferred organic reagent used in this step is a mixture of 2-hydroxy-5-t-nonyl acetophenoneoxime in aliphatic kerosene modified by the addition of iso-tridecanol. This reagent stream (27) enters mixer settler strip cells (A8), (A9) and (A10) where it is contacted with high strength ammoniacal ammonium carbonate liquor (28), typical composition 280 g/l ammonia and 230 g/l carbon dioxide, to remove nickel from the organic reagent. The nickel free organic reagent stream (29) now contacts the cobalt tetrammine rich ammoniacal liquor (26) in a series of 3 extract mixer settler units (A5), (A6) and (A7) to remove the nickel impurity from the cobalt liquor. A suitable organic to aqueous phase ratio may be 1:1 at an extract cell temperature of between 35° and 60°C and a strip cell temperature of between 35° and 55°C for a period of between 30 seconds and 30 minutes.

The cobalt tetrammine rich ammoniacal liquor (30) is then passed through two ion exchange columns in series (A11) and (A12) to lower calcium and magnesium impurities to acceptable levels.

In order to recover the cobalt as an intermediate, the cobalt tetrammine rich ammoniacal ammonium carbonate liquor (31) is delivered continuously under controlled conditions to a multi tray distillation column (A13) and heated with steam. The aqueous slurry (32) is pumped to a thickener (A14) to recover the suspended cobaltic oxide hydroxide solids prior to filtration through filter (A15) to produce a moist filter cake.

Claims

1. A process for the preparation and purification of a cobalt intermediate from a cobalt sulphate solution containing cationic and anionic impurities, including the successive steps of:
 - (i) reacting the cobalt sulphate solution with an organic reagent to extract unwanted cationic impurities from the sulphate solution;
 - (ii) extracting the cobalt from the sulphate solution with an organic reagent, to create a cobalt loaded organic phase substantially free of all anionic impurities;
 - (iii) stripping the cobalt loaded organic phase with a high strength ammoniacal ammonium carbonate solution, to create an ammoniacal ammonium carbonate strip liquor rich in cobalt II ammines;
 - (iv) converting the cobalt II ammines to cobalt III tetrammines;
 - (v) extracting the majority of nickel from the cobalt tetrammine rich ammoniacal liquor with a suitable organic reagent; and
 - (vi) recovering the cobalt from the cobalt tetrammine rich ammoniacal liquor.
2. A process according to claim 1, wherein further unwanted cationic impurities are extracted prior to the recovery step by contacting the cobalt tetrammine rich ammoniacal liquor with an ion exchange resin.
3. A process according to claim 1 or claim 2 wherein impure cobalt sulphide solids are solubilized prior to step (i) to form the cobalt sulphate solution.
4. A process according to any preceding claim wherein the cobalt sulphate solution has a pH of less than 2.5 and a cobalt concentration of from 30 to 90 g/l.
5. A process according to any preceding claim wherein the cobalt sulphate solution is treated with a strong oxidant to convert any iron impurities to ferric (Fe³⁺) ions prior to treating with the organic reagent of step (i).
6. A process according to any preceding claim wherein the organic reagent referred to in step (i) is a phosphinic acid derivative dissolved in a kerosene solvent and is specific for the extraction of ferric iron and zinc from the cobalt sulphate solution under controlled pH conditions.
7. A process according to claim 6, wherein the organic reagent is bis(2,4,4-trimethylpentyl)phosphinic acid in aliphatic kerosene.
8. A process according to any preceding claim wherein the pH of the solution for step (i) is maintained at an initial pH of from 2.1 to 2.6 to separate approximately 95% of the ferric iron from the cobalt sulphate solution and slowly raised to a pH of about 3.5, specific to separate zinc from the cobalt sulphate solution.
9. A process according to any preceding claim wherein the organic reagent used in step (ii) is a phosphoric acid derivative dissolved in kerosene and modified with an aliphatic long chain alcohol.
10. A process according to claim 9, wherein the organic reagent is a mixture of di(2-ethylhexyl) phosphoric acid, iso-tridecanol and aliphatic kerosene.

11. A process according to any preceding claim wherein substantially all the anionic impurities remain in the sulphate solution following step (ii), and the cobalt loaded organic phase is subjected to an aqueous scrub liquor to remove any residual anionic impurities that may have physically transferred to the organic phase.
- 5 12. A process according to any preceding claim wherein the cobalt is stripped from the cobalt loaded organic phase in step (iii) by a high strength ammoniacal ammonium carbonate solution having an ammonium content of from 205 to 330 g^l⁻¹ and a carbon dioxide content of from 160 to 300 g^l⁻¹.
13. A process according to claim 12, wherein the ammonium content is from 255 to 300 g^l⁻¹ and the carbon dioxide content is from 200 to 260 g^l⁻¹.
- 10 14. A process according to claim 13, wherein the ammonium content is about 285 g^l⁻¹ and the carbon dioxide content is about 230 g^l⁻¹.
- 15 15. A process according to any preceding claim wherein prior to extracting the nickel from the ammoniacal ammonium carbonate strip liquor, the concentration of cobalt II ammine in the strip liquor is lowered from 20 g^l⁻¹ to 50ppm by sparging the strip liquor with air, oxygen or hydrogen peroxide;
and the concentration of the uncomplexed ammonium is lowered by controlled distillation to 20-60 g^l⁻¹.
- 20 16. A process according to any preceding claim wherein the organic reagent of step (v) is an oxime reagent in kerosene and modified by the addition of a long chain aliphatic alcohol.
- 25 17. A process according to claim 16, wherein the organic reagent is selected from 2-hydroxy-5-1-nonyl acetophenone-oxime, 2-hydroxy-5-nonyl salicylaldoxime, alkyl, aryl and halide substituted beta diketones in an aliphatic or aromatic kerosene carrier, modified by an alcohol selected from iso-tridecanol, iso-undecanol, iso-dodecanol and the corresponding linear types.
- 30 18. A process according to claim 17, wherein the organic reagent is a mixture of 2-hydroxy-5-1-nonyl acetophenone-oxime in aliphatic kerosene, modified by the addition of iso-tridecanol.
- 35 19. A process according to claim 18, wherein prior to extracting nickel from the cobalt tetrammine rich ammoniacal liquor, any residual nickel is removed from the organic reagent by contacting the organic reagent with a high strength ammoniacal ammonium carbonate liquor having an ammonia content of from 205 to 330 g^l⁻¹ and a carbon dioxide content of from 160 to 300 g^l⁻¹.
- 40 20. A process according to claim 19, wherein the ammonia content is about 285 g^l⁻¹ and the carbon dioxide content is about 230 g^l⁻¹, and the reaction takes place in a series of mixer settler strip cells at a strip cell temperature of between 35° and 55°C for a period of between 30 seconds and 30 minutes in each cell.
- 45 21. A process according to any preceding claim wherein the cobalt tetrammine rich ammoniacal liquor is contacted with the organic reagent in a series of extract mixer settler units in an organic to aqueous ratio of from 0.2:1 to 5:1.
22. A process according to claim 21, wherein the cobalt rich tetrammine ammoniacal liquor is contacted with the organic reagent in an organic to aqueous ratio of from 1:1 to 2:1, for a period of between 30 seconds and 30 minutes in each extract cell, at an extract cell temperature of between 35° and 60°C.
- 50 23. A process according to claim 2, or any one of claims 3 to 22 when dependent on claim 2, wherein the ion exchange resin is a chelating ion exchange resin of the iminodiacetate type with a high affinity for calcium and magnesium in order to extract calcium and magnesium ions from the cobalt tetrammine rich ammoniacal liquor.
24. A process according to any preceding claim wherein cobalt is recovered from the cobalt tetrammine rich ammoniacal liquor as an intermediate by distilling the ammoniacal liquor with steam and pumping the aqueous slurry to a thickener to recover the suspended cobaltic oxide hydroxide solids.
- 55 25. A process according to claim 2, or any one of claims 3 to 24 when dependent on claim 2, wherein cobalt is recovered from the cobalt tetrammine rich ammoniacal liquor by treating the ammoniacal liquor exiting the ion exchange resin system in a reductive step by contacting the ammoniacal liquor with finely divided pure cobalt metal powder to reduce the cobalt III tetrammine to labile cobalt II ammine, in a inert atmosphere at a temperature from 25°C to

35°C, resulting in the precipitation of cobalt hydroxy carbonate solids.

26. A cobalt intermediate prepared by the process according to claim 1 or 2.

Patentansprüche

1. Verfahren zur Herstellung und Reinigung einer Kobaltzwischenverbindung aus einer Lösung von Kobaltsulfat, welche kationische und anionische Verunreinigungen enthält, umfassend die aufeinanderfolgenden Schritte:
 - (i) Umsetzen der Kobaltsulfatlösung mit einem organischen Reagenz, um die unerwünschten kationischen Verunreinigungen aus der Sulfatlösung zu extrahieren;
 - (ii) Extraktion des Kobalts aus der Sulfatlösung mit Hilfe eines organischen Reagenz, zur Erzeugung einer mit Kobalt beladenen organischen Phase, die im wesentlichen frei von allen anionischen Verunreinigungen ist;
 - (iii) Ausziehen der mit Kobalt beladenen organischen Phase mit einer konzentrierten Ammoniumcarbonatlösung, zur Erzeugung einer ammoniakalischen Ammoniumcarbonatphase, die reich an Kobalt(II)aminen ist;
 - (iv) Überführung der Kobalt(II)amine in Kobalt(III)tetramine;
 - (v) Extraktion des überwiegenden Anteils an Nickel aus der ammoniakalischen, an Kobalttetramin reichen Phase mit einem geeigneten organischen Reagenz; und
 - (vi) Zurückgewinnung des Kobalts aus der ammoniakalischen, an Kobalttetramin reichen Phase.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß vor dem Schritt der Rückgewinnung weitere unerwünschte kationische Verunreinigungen entfernt werden, indem die an Kobalttetramin reiche, ammoniakalische Phase mit einem Ionenaustauscherharz in Berührung gebracht wird.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß vor dem Schritt (i) verunreinigte feste Kobaltsulfide unter Ausbildung einer Kobaltsulfatlösung in Lösung gebracht werden.
4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Kobaltsulfatlösung einen pH von weniger als 2,5 und eine Kobaltkonzentration zwischen 30 und 90 g/l aufweist.
5. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Kobaltsulfatlösung vor der in Schritt (i) erfolgenden Behandlung mit dem organischen Reagenz mit einem starken Oxidationsmittel behandelt wird, um jegliche Verunreinigung durch Eisen in Eisen(III)-Ionen (Fe^{3+}) zu überführen.
6. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das in Schritt (i) genannte organische Reagenz ein Derivat einer hypophosphorigen Säure ist, das in einem Petrolether als Lösungsmittel gelöst ist und bei bestimmten pH-Bedingungen spezifisch für die Extraktion von Eisen-(III)-Ionen und Zinkionen aus der Kobaltsulfatlösung ist.
7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das organische Reagenz bis-(2,4,4-trimethylpentyl) hypophosphorige Säure in aliphatischem Petrolether ist.
8. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der pH der Lösung aus Schritt (i) bei einem Anfangs-pH zwischen 2,1 und 2,6 gehalten wird, um annähernd 95 % der Eisen-(III)-Ionen aus der Kobaltsulfatlösung zu entfernen, und dann langsam auf einen pH von ungefähr 3,5 erhöht wird, um spezifisch Zink aus der Kobaltsulfatlösung zu entfernen.
9. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das in Schritt (ii) verwendete organische Reagenz ein Derivat der hypophosphorigen Säure ist, das in Petrolether gelöst ist und mit einem langkettigen aliphatischen Alkohol modifiziert ist.
10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das organische Reagenz eine Mischung aus Di-

(2-ethylhexyl)-hypophosphoriger Säure, iso-Tridecanol und aliphatischem Petrolether ist.

- 5 11. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß alle anionischen Verunreinigungen im wesentlichen in der in Schritt (ii) erhaltenen Sulfatlösung verbleiben, und die mit Kobalt beladene organische Phase mit einer wäßrigen Waschlösung gewaschen wird, um alle verbleibenden anionischen Verunreinigungen, die in die organische Phase übergetreten sind, zu entfernen.
- 10 12. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß in Schritt (iii) das Kobalt aus der mit Kobalt beladenen organischen Phase mit einer konzentrierten ammoniakalischen Lösung von Ammoniumcarbonat entfernt wird, die einen Ammoniakgehalt zwischen 205 und 330 g/l und einen Kohlendioxidgehalt zwischen 160 und 300 g/l aufweist.
- 15 13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß der Ammoniumgehalt zwischen 255 und 300 g/l und der Kohlendioxidgehalt zwischen 200 und 260 g/l beträgt.
- 20 14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß der Ammoniumgehalt ungefähr 285 g/l und der Kohlendioxidgehalt ungefähr 230 g/l beträgt.
- 25 15. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß vor der Extraktion des Nickels aus der ammoniakalischen ammoniumcarbonathaltigen Extraktionsflüssigkeit die Konzentration des Kobalt-(II)-amins in der Extraktionsflüssigkeit von 20 g/l auf 50 ppm erniedrigt wird, indem die Extraktionsflüssigkeit mit Luft, Sauerstoff oder Wasserstoffperoxid behandelt wird; und die Konzentration an nicht komplexiertem Ammonium durch Destillation auf 20 - 60 g/l erniedrigt wird.
- 30 16. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das organische Reagenz in Schritt (v) ein Oximreagenz ist, das in Petrolether gelöst und durch die Zugabe eines langkettigen aliphatischen Alkohols modifiziert ist.
- 35 17. Verfahren nach Anspruch 16, dadurch gekennzeichnet, daß das organische Reagenz aus der von 2-Hydroxy-5-t-nonyl-Acetophenonoxim, 2-Hydroxy-5-t-nonyl-Salicylaldoxim, alkyl-, aryl- und halogensubstituierten β -Diketonen, gelöst in einem aliphatischen oder aromatischen Petrolethercarrier, gebildeten Gruppe ausgewählt ist, das mit einem Alkohol modifiziert ist, der aus der von iso-Tridecanol, iso-Undecanol, iso-Dodecanol und den entsprechenden geradkettigen Isomeren gebildeten Gruppe ausgewählt ist.
- 40 18. Verfahren nach Anspruch 17, dadurch gekennzeichnet, daß das organische Reagenz eine Mischung von 2-Hydroxy-5-t-nonyl-Acetophenonoxim in aliphatischem Petrolether ist, die durch Zugabe von iso-Tridecanol modifiziert ist.
- 45 19. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß vor der Extraktion des Nickels aus der an Kobalttetramin reichen ammoniakalischen Phase restliches Nickel aus dem organischen Reagenz entfernt wird, indem das organische Reagenz mit einer konzentrierten Ammoniumcarbonatlösung behandelt wird, die einen Ammoniumgehalt von 205 bis 330 g/l und einen Kohlendioxidgehalt von 160 bis 300 g/l aufweist.
- 50 20. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß der Ammoniumgehalt ungefähr 285 g/l und der Kohlendioxidgehalt ungefähr 230 g/l ist, und die Reaktion in einer Reihe von Mischer-Scheider-Extraktionszellen bei einer Temperatur der Extraktionszellen von 35 ° bis 55 °C für eine Dauer von 30 Sekunden bis 30 Minuten pro Zelle durchgeführt wird.
- 55 21. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die an Kobalttetramin reiche ammoniakalische Phase mit dem organischen Reagenz in einer Reihe von Mischer-Scheider-Extraktionseinheiten umgesetzt wird, wobei das Verhältnis von organischer zu wäßriger Phase zwischen 0,2 : 1 und 5 : 1 beträgt
22. Verfahren nach Anspruch 21, dadurch gekennzeichnet, daß die an Kobalttetramin reiche ammoniakalische Phase mit dem organischen Reagenz für eine Dauer von 30 Sekunden bis 30 Minuten je Extraktionszelle und bei einer Temperatur der Extraktionszelle von 35 ° bis 60 °C behandelt wird, wobei das Verhältnis von organischer zu wäßriger Phase zwischen 1:1 und 2:1 beträgt.
23. Verfahren nach Anspruch 2 oder einem der auf Anspruch 2 rückbezogenen Ansprüche 3 bis 22, dadurch gekennzeichnet,

zeichnet, daß der Ionenaustauscher ein chelatbildender Ionenaustauscher vom Iminodiacetattyp mit einer hohen Affinität zu Calcium oder Magnesium ist, wodurch die Calcium- und Magnesiumionen aus der an Kobalttetramin reichen ammoniakalischen Phase entfernt werden.

- 5 24. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Kobalt aus der an Kobalttetramin reichen ammoniakalischen Phase als Zwischenprodukt wiedergewonnen wird, indem die ammoniakalische Phase mit Wasserdampf destilliert wird und die wäßrige Aufschlämmung zur Rückgewinnung der niedergeschlagenen basischen Kobaltoxide in einen Eindicker überführt wird.
- 10 25. Verfahren nach Anspruch 2 oder einem der auf Anspruch 2 rückbezogenen Ansprüche 3 bis 24, dadurch gekennzeichnet, daß das Kobalt aus der an Kobalttetramin reichen ammoniakalischen Phase zurückgewonnen wird, indem die aus dem Ionenaustauscherharzsystem austretende ammoniakalische Phase einem reduktiven Schritt unterzogen wird, wobei die ammoniakalische Phase in einer inerten Atmosphäre bei einer Temperatur von 25 °C bis 35 °C mit feinverteiltem reinem Kobaltmetallpulver versetzt wird, um unter Präzipitation von festem Kobalthydroxycarbonat das Kobalt-(III)-tetramin zu instabilem Kobalt-(II)-amin zu reduzieren.
- 15 26. Kobaltzwischenverbindung, erhältlich durch das Verfahren nach einem der Ansprüche 1 oder 2.

20 Revendications

1. Un procédé pour la préparation et la purification d'un composé intermédiaire de cobalt à partir d'une solution de sulfate de cobalt, qui renferme des impuretés cationiques et anioniques, comportant les étapes successives de :
- 25 (i) faire réagir la solution de sulfate de cobalt avec un réactif organique afin d'extraire les impuretés cationiques non souhaitées de la solution de sulfate ;
 (ii) extraire le cobalt de la solution de sulfate avec un réactif organique afin de réaliser une phase organique chargée au cobalt, essentiellement exempte de la totalité des impuretés anioniques ;
 30 (iii) laver la phase organique chargée de cobalt avec une solution de carbonate d'ammonium fortement ammoniacale, afin de réaliser une liqueur de lavage ammoniacale de carbonate d'ammonium, riche en ammines cobalteuses ;
 (iv) convertir les ammines cobalteuses en tétrammines cobaltiques ;
 (v) extraire la majorité du nickel de la liqueur ammoniacale riche en tétrammine de cobalt au moyen d'un réactif organique approprié ; et
 35 (vi) récupérer le cobalt de la liqueur ammoniacale riche en tétrammine de cobalt.
2. Un procédé selon la revendication 1, dans lequel d'autres impuretés cationiques non souhaitées sont extraites avant l'étape de récupération en mettant en contact la liqueur ammoniacale riche en tétrammine de cobalt, avec une résine échangeuse d'ions.
- 40 3. Un procédé selon la revendication 1 ou la revendication 2, dans lequel les produits impurs à base de sulfure de cobalt sont solubilisés avant l'étape (1) afin de former une solution de sulfate de cobalt.
4. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la solution de sulfate de cobalt possède un pH inférieur à 2,5 et une concentration en cobalt de 30 à 90 g^t.
 45 5. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la solution de sulfate de cobalt est traitée avec un agent oxydant fort afin de convertir des impuretés quelconques à base de fer en ions ferriques (Fe³⁺) avant le traitement avec le réactif organique de l'étape (i).
- 50 6. Un procédé selon l'une quelconque des revendication précédentes, dans lequel le réactif organique auquel on se réfère à l'étape (i) est un dérivé de l'acide phosphinique, dissous dans un solvant de type kérosène, et est spécifique pour l'extraction du fer ferrique et du zinc de la solution de sulfate de cobalt sous des conditions de pH contrôlé.
- 55 7. Un procédé selon la revendication 6, dans lequel le réactif organique est de l'acide bis(2,4,4-triméthylpentyl)phosphonique dans du kérosène aliphatique.
8. Un procédé selon l'une des revendications précédentes, dans lequel le pH de la solution pour l'étape (i) est main-

tenu à un pH initial de 2,1 à 2,6 afin de séparer approximativement 95 % du fer ferrique de la solution de sulfate de cobalt et est lentement portée à un pH d'environ 3,5, spécifique pour séparer le zinc de la solution de sulfate de cobalt.

- 5 9. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le réactif organique utilisé à l'étape (ii) est un dérivé de l'acide phosphorique, dissous dans du kérosène et modifié au moyen d'un alcool aliphatique à longue chaîne.
- 10 10. Un procédé selon la revendication 9, dans lequel le réactif organique est un mélange d'acide di(2-éthylhexyl) phosphorique, d'iso-tridécanol et de kérosène aliphatique.
- 15 11. Un procédé selon l'une quelconque des revendications précédentes, dans lequel essentiellement la totalité des impuretés anioniques restent dans la solution de sulfate à la suite de l'étape (ii), et la phase organique chargée en cobalt est soumise à une liqueur aqueuse de lavage afin d'éliminer les impuretés anioniques résiduelles quelconques qui peuvent avoir été physiquement transférées dans la phase organique.
- 20 12. Un procédé selon l'une quelconque des revendications précédentes dans lequel le cobalt est éliminé par lavage de la phase organique chargée de cobalt dans l'étape (iii) à l'aide d'une solution fortement ammoniacale de carbonate de sodium, présentant une teneur en ammonium de 205 à 330 g^t⁻¹ et une teneur en dioxyde de carbone de 160 à 300 g^t⁻¹.
- 25 13. Un procédé selon la revendication 12, dans lequel la teneur en ammonium se situe de 255 à 300 g^t⁻¹ et la teneur en dioxyde de carbone se situe de 200 à 260 g^t⁻¹.
- 30 14. Un procédé selon la revendication 13, dans lequel la teneur en ammonium est d'environ 285 g^t⁻¹ et la teneur en dioxyde de carbone est d'environ 230 g^t⁻¹.
- 35 15. Un procédé selon l'une quelconque des revendications précédentes, dans lequel, avant d'extraire le nickel de la liqueur ammoniacale lavée au carbonate d'ammonium, la concentration d'amine cobalteuse dans la liqueur de lavage est abaissée de 20 g^t⁻¹ à 50 ppm par aspersion de la liqueur de lavage avec de l'air, de l'oxygène ou du peroxyde d'hydrogène ;
et la concentration de l'ammonium non complexé est abaissée par distillation contrôlée jusqu'à 20-60 g^t⁻¹.
- 40 16. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le réactif organique de l'étape (v) est un réactif de type oxime dans du kérosène et est modifié par l'addition d'un alcool aliphatique à longue chaîne.
- 45 17. Un procédé selon la revendication 16, dans lequel le réactif organique est choisi parmi le 2-hydroxy-5-t-nonyl acétophénoneoxime, le 2-hydroxy-5-nonyl salicylaldoxime, des bêta-dicétones à substitution alkyle, aryle et halogénure dans un support à base de kérosène aliphatique ou aromatique, modifié par un alcool choisi parmi l'iso-tridécanol, l'iso-undécanol, l'iso-dodécanol et les types linéaires correspondants.
- 50 18. Un procédé selon la revendication 17, dans lequel le réactif organique est un mélange de 2-hydroxy-5-t-nonyl acétophénoneoxime dans du kérosène aliphatique, modifié par l'addition d'iso-tridécanol.
- 55 19. Un procédé selon la revendication 18, dans lequel, avant l'extraction nickel de la liqueur ammoniacale riche en tétrammine de cobalt, du nickel résiduel est éliminé du réactif organique en mettant en contact le réactif organique avec une liqueur de carbonate d'ammonium, fortement ammoniacale, qui présente une teneur en ammoniac de 205 à 300 g^t⁻¹ et une teneur en dioxyde de carbone de 160 à 300 g^t⁻¹.
20. Un procédé selon la revendication 19, dans lequel la teneur en ammoniac est d'environ 285 g^t⁻¹ et la teneur en dioxyde de carbone est d'environ 230 g^t⁻¹, et la réaction est mise en oeuvre dans une série de cellules de lavage du type mélangeur-décanteur pour une température de la cellule de lavage se situant entre 35° et 55°C pendant une période entre 30 secondes et 30 minutes dans chaque cellule.
21. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la liqueur ammoniacale riche en tétrammine de cobalt est mise en contact avec le réactif organique dans une série d'appareils d'extraction du type mélangeur-décanteur selon un rapport phase organique/ phase aqueuse de 0,2:1 à 5:1.

EP 0 651 062 B1

22. Un procédé selon la revendication 21, dans lequel la liqueur ammoniacale riche en tétrammine de cobalt est mise en contact avec le réactif organique selon un rapport phase organique/phase aqueuse de 1:1 à 2:1, pendant une période se situant entre 30 secondes et 30 minutes dans chaque cellule d'extraction, à une température de la cellule d'extraction se situant entre 35° et 60°C.

23. Un procédé selon la revendication 2 ou bien l'une quelconque des revendications 3 à 22 lorsqu'elles dépendent de la revendication 2, dans lequel la résine échangeuse d'ions est une résine échangeuse d'ions chélatants du type iminodiacétate avec une forte affinité pour le calcium et le magnésium afin d'extraire les ions calcium et magnésium de la liqueur ammoniacale riche en tétrammine de cobalt.

24. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le cobalt est récupéré de la liqueur ammoniacale riche en tétrammine de cobalt sous la forme d'un produit intermédiaire en distillant la liqueur ammoniacale à la valeur et en pompant la suspension aqueuse pour la transférer dans un dispositif épaisseur afin de récupérer les produits solides du type hydroxyde-oxyde cobaltique en suspension.

25. Un procédé selon la revendication 1 ou l'une quelconque des revendications 3 à 24 lorsqu'elles dépendent de la revendication 2, dans lequel le cobalt est récupéré de la liqueur ammoniacale riche en tétrammine de cobalt en traitant la liqueur ammoniacale provenant du système de résine échangeuse d'ions dans une étape de réaction en mettant en contact la liqueur ammoniacale avec une poudre métallique de cobalt pur, finement divisé, afin de réduire la tétrammine cobaltique en ammine cobalteuse labile, dans une atmosphère inerte à une température de 25°C à 35°C, ce qui se traduit par la précipitation des produits solides du type hydroxy-carbonate de cobalt.

26. Un composé intermédiaire de cobalt, préparé par le procédé selon les revendications 1 ou 2.

